

Excited State Structure by Time-Resolved X-Ray Diffraction at the SUNY X3 Beamline at NSLS

P. Coppens,¹ G. Wu,² C.D. Kim,¹ S. Pillet,¹ I. Novozhilova,¹ and W.K. Fullagar²

¹SUNY at Buffalo

²Beamline X3, NSLS, Brookhaven National Laboratory

Conventional X-ray crystallography has traditionally been limited to the study of the ground-state structure of molecules and solids. This limitation is now being removed by the availability of synchrotron sources and the rapid advances in laser and detector technology. This means that it is becoming possible to study dynamical processes in solids. Foremost among these are the photo-induced generation of electronically excited states, which tend to be highly reactive and act as intermediates in chemical reactions.

In a first application of time-resolved monochromatic single crystal methods, we have used a stroboscopic technique [1], in which the molecule is repeatedly excited, and the structural change probed for a

period of microseconds immediately after each of as many as 5000 excitations per second (Fig. 1), to study the change in geometry of tetrakis(pyrophosphito)dipalladium(II) ($\text{Pt}_2(\text{pop})_4^{4-}$ ion, $\text{pop} = [\text{HO}(\text{O})\text{POP}(\text{O})\text{OH}]^{2-}$, Fig. 2). In order to increase the fraction of the X-ray photons effectively used in the experiment, X-ray pulses are produced by inserting a rotating chopper wheel in the X-ray beam, rather than by using the pulsed structure of the synchrotron source. The use of this method is related to the mismatch between the pulse frequencies of sufficiently powerful lasers and the synchrotron source, which would reduce the duty cycle to an unacceptable value.

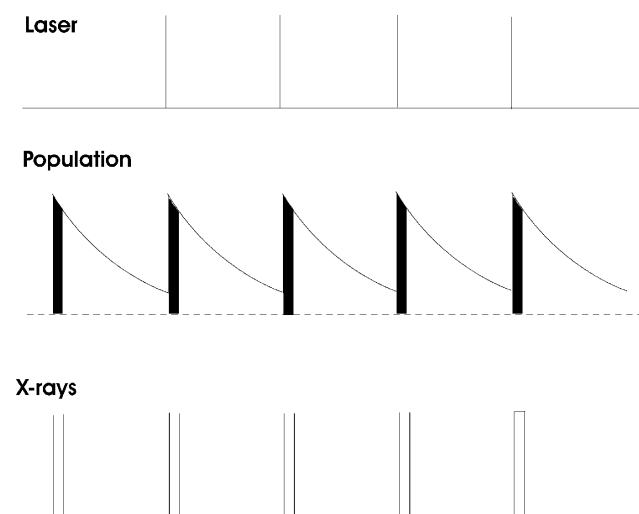


Figure 1. Schematic of the time structure of the stroboscopic X-ray experiment. For the experimental frequency of 5100 Hz the spacing between adjacent maxima is 196 μsec . The width of the X-ray pulse in the experiment is 33 μsec .

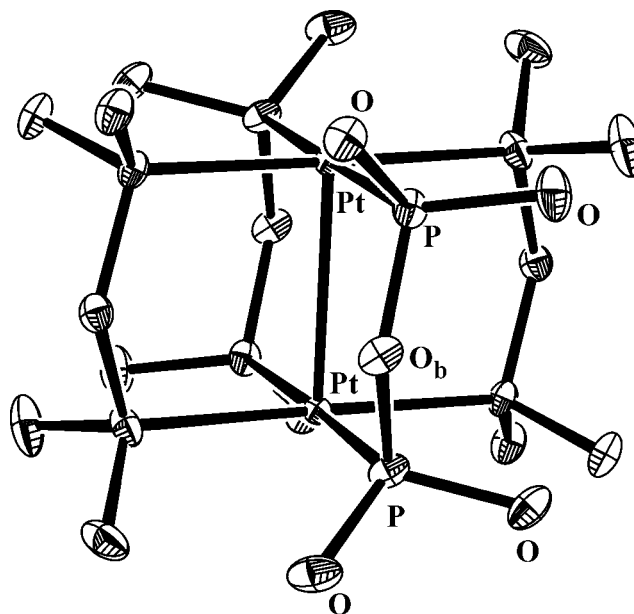


Figure 2. ORTEP diagram of the $(\text{Pt}_2(\text{pop})_4)^{4-}$ ion, $\text{pop} = [\text{HO}(\text{O})\text{POP}(\text{O})\text{OH}]^{2-}$ at 17 K. 50% probability ellipsoids. O_b indicates the bridging oxygen atom.

In the experiment performed, the frequency and X-ray pulse width were 5100 Hz and 33 μ s respectively, with an X-ray duty cycle of 17%. During the experiment, pulses from a tripled Nd/YAG pump laser ($\lambda=355$ nm) are synchronized with the X-ray pulses. The light from the Nd/YAG pump laser is guided through a tapered optical fiber and focused on a sample of 50 μ m linear dimension, kept at a temperature of 17 K by means of a helium gas flow.

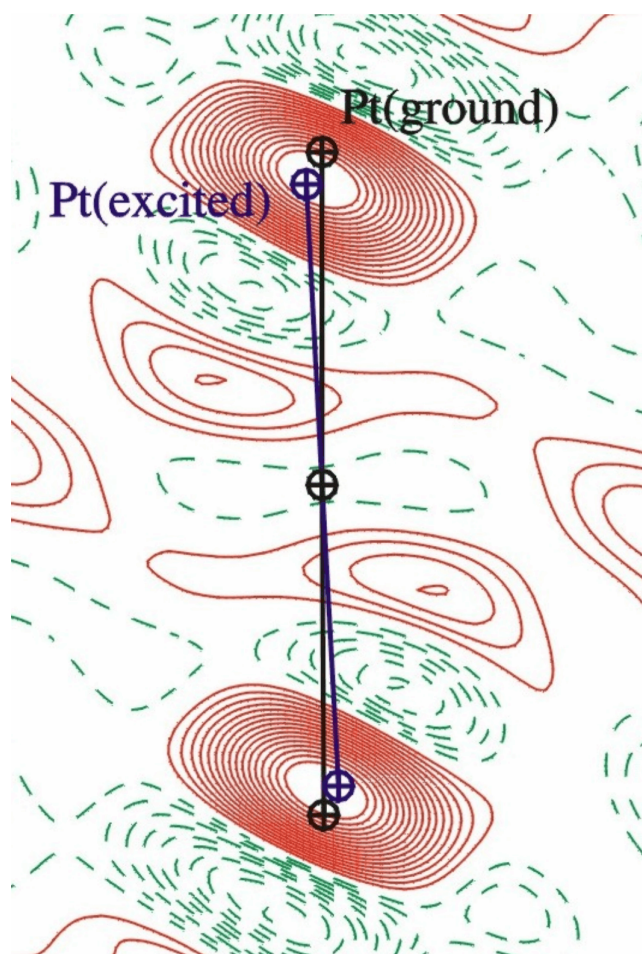


Figure 3. Photodifference map in the plane of the Pt-Pt bond bisecting two Pt-P vectors. A center of symmetry is located at the circle in the center of the drawing. Red lines positive, green lines negative. Contours at 0.1 electrons/ \AA^3 .

In the experiment [2], a large number of frames of data are collected with an area detector, each covering a 0.3° rotation of the sample. For every frame, light-on data collection alternates with light-off measurement over the same 0.3° rotation range. Minimization of the time delay between the on- and off-measurements provides essentially identical conditions during light-on and light-off data collection, and significantly increases the sensitivity of the experiment.

The light-induced structural changes are illustrated by a *photodifference* map (Fig. 3), which shows the change in electron density upon light exposure. It is obtained by Fourier summation with coefficients equal to the difference between the 'on' and 'off' structure factors. The map gives clear evidence for a displacement of the Pt atoms in a direction towards the other Pt atom in the molecular ion. The direction of the displacement does not coincide exactly with the intra-molecular Pt-Pt vector, indicating that a small molecular rotation accompanies the shortening of the Pt-Pt bond on excitation. Though quantitative analysis of the results shows the excited state population to be only 2% of the total number of molecules in the crystal, a significant Pt-Pt bond shortening on excitation of 0.28(9) \AA is obtained, in agreement with the proposed mechanism of excitation, in which a Pt-Pt anti-bonding $d\sigma^*$ electron migrates to a weakly-bonding $p\sigma$ orbital of the lowest unoccupied molecular orbital (LUMO). These results agree well with values derived from analysis of spectroscopic data.

The results serve as a test for theoretical calculations of the excited state geometry, which is quite dependent on the nature of the calculation. Values of the excited state Pt-Pt bond length, predicted by a series of calculations performed to complement the experiments, range from 0.15-0.58 \AA , even though the ordering of the molecular orbitals is the same according to all calculations. The HOMO and LUMO orbitals are illustrated in Fig. 4. Interestingly, the calculations that give the best excited-state geometry are not those that best reproduce the ground state structural parameters.

The stroboscopic time-resolved diffraction method is applicable to reversible light-driven processes in the crystalline state, including solids in which photoactive molecules are embedded in three-dimensionally ordered supra-molecular crystals. As the method can be applied to many systems, including molecules and molecular assemblies involved in photosynthetic reactions, vision and energy storage, further applications providing insight into a wide range of dynamic processes may be anticipated.

Acknowledgments

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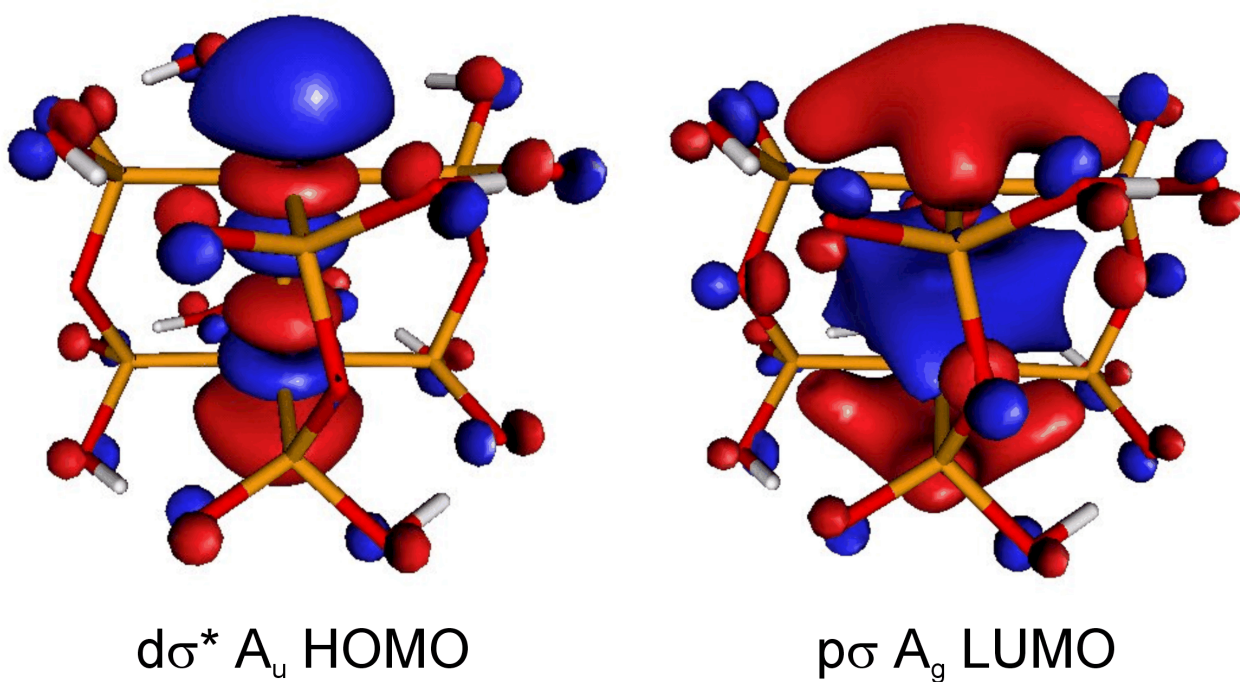


Figure 4. HOMO and LUMO levels of the $(Pt_2(pop)_4)^{4-}$ ion, from Density Functional Theory calculations.